Controlled Nanoparticle Metal Phosphates (Metal = Al, Fe, Ce, and Sr) Coatings on LiCoO$_2$ Cathode Materials

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Despite the fact that the same coating concentration and annealing temperature are used for MPO$_4$ nanoparticle coatings (M = Al, Fe, Ce, and SrH) on a LiCoO$_2$ cathode, the extent of the coating coverage is influenced by the nanoparticle size or morphology. Nanoparticles (AlPO$_4$ or FePO$_4$) with a size smaller than 20 nm led to the complete encapsulation of LiCoO$_2$, but those with sizes greater than 150 nm (CePO$_4$) or with whisker shapes (SrHPO$_4$) led to partial encapsulation. This difference affected the discharge capacity. The LiCoO$_2$ completely encapsulated with AlPO$_4$ or FePO$_4$ showed the highest discharge capacity of 230 mA/h/g at 4.8 and 3 V at a rate of 0.1 C (=18 mA/g), which diminished with decreasing coating coverage in the order of Al > Fe > SrH < Ce < bare cathode. However, the capacity retention during cycling increased in the order of Al > Ce > SrH > Fe > bare cathode. This is consistent with the capacity retention result obtained at 90°C storage for 4 h.

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Experimental

The MPO$_4$ nanoparticles (M = Al, Fe, SrH, and Ce) were prepared from a direct reaction between M nitrate and (NH$_4$)$_2$HPO$_4$ in distilled water M nitrate (3 g) and (NH$_4$)$_2$HPO$_4$ (1 g) were dissolved in water (25 g), and the rapid formation of white precipitates could be observed. For X-ray diffraction (XRD) and transmission electron microscopy (TEM), the precipitates were centrifuged at 3000 rpm for 5 min, which was followed by drying and annealing at 130 and 700°C for 5 h, respectively. To coat the 10 μm sized LiCoO$_2$ cathode (100 g), cathode powders were added to the coating solution with constant stirring, which was followed by drying and annealing at 130 and 700°C for 10 and 5 h, respectively. Based upon mass spectroscopy (MS), the coating mass ratio was estimated to be 0.01 g of the coating per gram of LiCoO$_2$. The coin-type half cell consists of a cathode (94 wt %), a Li metal anode, and a separator, and the electrolyte for coin-type half cells (2016 type) was 1 M LiPF$_6$ with ethylene carbonate/diethyl carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (30:30:40 vol %) (Cheil Industries, Korea). The loading level of LiCoO$_2$ studied per square cm was 35 mg. The cells for the cycling tests were tested at a charge-cutoff voltage of 4.8 V.

In 1996, Bellcore patented an Al$_2$O$_3$, B$_2$O$_3$, and SiO$_2$ coating on spinel LiMn$_2$O$_4$ to suppress Mn dissolution from LiMn$_2$O$_4$ at elevated temperatures. However, it was found that the irreversible capacity and capacity retention of the coated sample was inferior to the bare sample despite the lower Mn dissolution rate at 55°C storage. They reported the examples of B$_2$O$_3$-coated spinel at elevated temperature only, and there was no explanation for the decreasing capacity retention after the coating, compared with the bare cathode. Such deteriorated behavior of the coated cathode may be associated with the formation of a thick coating layer that impedes the Li diffusivity. To overcome these problems, LiCoO$_2$, which has a strong resistance to HF, was coated on the LiMn$_2$O$_4$ and showed improved capacity retention and lower irreversible capacity during cycling at 55°C. On the other hand, LiMn$_2$O$_4$ was coated on LiCoO$_2$ to improve the thermal stability of the delithiated LiCoO$_2$. Accordingly, SnO$_2$, Al$_2$O$_3$, ZrO$_2$, and TiO$_2$ coatings on LiCoO$_2$ and LiNi$_{1-x}$M$_x$O$_2$ via the solgel method have been intensively investigated. Among these coating materials, ZrO$_2$ coating exhibited the best capacity retention >4.5 V cycling, and high-temperature storage at 90°C. This finding was confirmed by Kim et al., and among the ZrO$_2$, Al$_2$O$_3$, and SiO$_2$ coatings, the ZrO$_2$ coating on LiMn$_2$O$_4$ had to the lowest capacity fading at 55°C cycling. This improvement was due to the fact that ZrO$_2$ behaves as an effective HF scavenger. Overall, these studies revealed that the physical morphology of the coating materials significantly influenced the electrochemical properties.

Metal phosphates (M = metal ion) are of great interest for many applications, for example, as molecular sieves or size-selective catalysts, catalyst supports, or optical materials, and their application have varied depending on the pore size, particle size, and metal ions. Dong et al. prepared mesoporous AlPO$_4$ by templating AlCl$_3$ and triethylphosphate with carbon spheres with a particle size of ~100 nm, which was removed by calcining at 550°C. Riwotski et al. reported the liquid-phase synthesis of La-, Ce-, and Te-doped LaPO$_4$ nanoparticles. In addition, they reported that higher boiling coordinating solvents such as triethylenediamine as a phosphate under nitrogen for 16 h at 200°C yielded ~8 nm sized nanocrystals with an irregular 0-D. Recently, the synthesis and electrochemical properties of AlPO$_4$ nanocrystals have attracted considerable interest because they have been considered to be potentially useful active coating materials for lithium intercalation compounds in Li secondary batteries. Recently, we found that AlPO$_4$-coated LiCoO$_2$ improved not only the 12 V overcharge stability, but also the cycling property at 4.8 V.  

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The cycle-life tests were proceeded by charging and discharging at 0.1 C for the first two cycles, which was followed by a cycle at 0.2 C, a cycle at 0.5 C, and finally a cycle at 1 C (current density 180 mA/g) for 46 cycles. The galvanostatic intermittent titration technique (GITT) was used to estimate the Li diffusivity, and the Li/LiCoO₂ test cells after finishing each 10 cycles were allowed to reach equilibrium at 4.3 V. To measure the capacity retention at 90°C, fresh cells Li/LiCoO₂ were charged to 4.6 and 4.8 V and stored at 90°C for 4 h, which was then cooled to room temperature. The cells were then discharged to 3 V at a rate of 0.2 C. The Co and metal ion dissolution (M = Al, Fe, Sr, and Ce) from the bare and coated LiCoO₂ cathodes was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and the electrolytes were obtained from the cycled cells using a centrifugal separation method. The nanoparticles and coated LiCoO₂ were characterized by XRD using Cu Kα radiation in the 2θ range, 15-70°.

Results and Discussion
Figure 1 shows TEM images of the MPO₄ nanoparticles prepared in water. The particle size of the AlPO₄ nanoparticles was <5 nm, which was the smallest among the MPO₄ nanoparticles. On the other hand, FePO₄ had a larger particle size of ~20 nm while CePO₄ and SrHPO₄ were found as whisker- and spherical-type (with a particle size of 150-200 nm) nanoparticles, respectively. This indicates that the particle size and morphology was governed by the metal ion. Figure 2 shows a comparison of the XRD patterns of the precipitated nanoparticles. The XRD patterns of the AlPO₄ and CePO₄ (M = Al and Ce) particles confirmed the presence of the orthorhombic (JCPDS no. 48-652) and monoclinic phases (JCPDS no. 4-632), respectively. However, that of the FePO₄ shows the formation of amorphous phase. ICP-MS analysis confirmed that the stoichiometry of Fe and P was 1:1, i.e., the formation of FePO₄. After heat-treatment at 700°C, the XRD patterns of AlPO₄, FePO₄, and SrHPO₄-coated LiCoO₂ (Fig. 3) showed only the LiCoO₂ phase, indicating that the coating was too thin to observe while that of the CePO₄-coated LiCoO₂ revealed the presence of crystalline CeO₂ phase. In the case of the AlPO₄-coated cathode, the coating thickness was estimated to be 10-15 nm. The XRD diffraction patterns of the isolated CePO₄ and SrHPO₄ particles after heat-treatment at 700°C revealed the presence of monoclinic CePO₄ (JCPDS no. 32-199), and an orthorhombic Sr₃P₂O₇ phase (JCPDS no. 24-1011), respectively (Fig. 4). The crystal structure of the coating layer is expected to be different from that of the isolated coating particle because MPO₄ might react with Li and even Co from the LiCoO₂ during annealing at 700°C, and transform into a new phase with an intrinsic stress in the nanoscale-coating layer. Hence, it is difficult to identify the coating layer phase. Despite this, the identification of the CeO₂ phase in the coated cathode suggests the existence of a completely isolated large portion of the particles from the coated cathode (this might be attributed to the partially decomposed CePO₄ in LiCoO₂ during annealing at 700°C). However, there was no secondary phase observed in the XRD pattern of the SrHPO₄-coated cathode, which indicates that a larger portion of the LiCoO₂ than CePO₄-coated cathode may be covered with the coating material. Electron probe microanalysis (EPMA) was performed to check the degree of encapsulation of the coated cathodes. Figure 5 shows the Co, M, and P mapping across the cross-sectioned LiCoO₂ particles. In the case of the AlPO₄ and FePO₄-coated LiCoO₂, Al and Fe elements were completely encapsulated on the particle surface in contrast to the Sr and Ce elements with the noncoating layers. On the other hand, the entire encapsulation of the cathode using the sol-gel driven Al₂O₃ and ZrO₂ coating.
was difficult to achieve. Another problem with a sol-gel coating is that it cannot control the coating thickness. For example, the TEM images reported by Thackeray’s group and Dahn’s group showed such evidence.\(^{14,32-34}\) However, the nanoparticle coating exhibited very good coating coverage and coating thickness could be controlled by the nanoparticle size.

The EPMA result is well consistent with the TEM images of the MPO\(_4\) -coated LiCoO\(_2\) (Fig. 6), and the FePO\(_4\) -coated LiCoO\(_2\) shows a completely covered coating layer with a thickness of \(-25\) -50 nm, which is thicker than the AlPO\(_4\) -coated LiCoO\(_2\) (\(-15\) -20 nm).\(^{35}\) This is due to the larger FePO\(_4\) particles than AlPO\(_4\), even though the same coating concentration (1 wt %) was used. In the case of CePO\(_4\) and SrHPO\(_4\), only a portion of the LiCoO\(_2\) was

Figure 4. XRD patterns of the isolated CePO\(_4\) and SrHPO\(_4\) nanoparticles after annealing at 700°C. Note the phase change of SrHPO\(_4\) to Sr\(_2\)P\(_2\)O\(_7\) after annealing.

Figure 5. EPMA of cross section MPO\(_4\)-coated LiCoO\(_2\) cathodes.

Figure 6. TEMs of (a-c) MPO\(_4\)-coated LiCoO\(_2\) (M = Fe, SrH, and Ce). (d) is a SAD pattern of CePO\(_4\)-coated LiCoO\(_2\).
covered with the particles. However, it is interesting to note that the original whisker type particle morphology of the CePO\textsubscript{4} was completely changed into an aggregation of \textasciitilde 30-40 nm sized particles. Selected area diffraction (SAD) of the coating particle of the CePO\textsubscript{4}-coated LiCoO\textsubscript{2} confirmed the presence of a CePO\textsubscript{4} phase that did not transform into the other phases from the interfacial reaction. This indicates that CePO\textsubscript{4} is inert. However, the crystal structure of the SrHPO\textsubscript{4}-coated cathode showed mixed phases with several different structures. As mentioned above, the observation of a secondary CeO\textsubscript{2} phase in the XRD pattern of the CePO\textsubscript{4}-coated cathode may result from the isolated particles. Therefore, a portion of the completely isolated Sr\textsubscript{2}P\textsubscript{2}O\textsubscript{7} and CeO\textsubscript{2} particles from the coated LiCoO\textsubscript{2} should exist in the LiCoO\textsubscript{2} particles.

Such partial encapsulation is related to the BET surface area of the nanoparticles, and the values for M = Al, Fe, SrH, and Ce correspond to 25, 16, 8, and 3 m\textsuperscript{2}/g, respectively. Because the nanoparticles adsorbed on the cathode are only possible through the physical bonding during the drying process at 130°C, those with a higher BET surface area should have a larger wetting area on the LiCoO\textsubscript{2}. Hence, there is no doubt that the AlPO\textsubscript{4} and FePO\textsubscript{4} particles can easily wet the LiCoO\textsubscript{2}, compared with SrHPO\textsubscript{4} and CePO\textsubscript{4}. On the other hand, the physical bonding was hardened via a chemical reaction between the Li in LiCoO\textsubscript{2} during annealing at 700°C. Figure 7 shows voltage profiles of the MPO\textsubscript{4}-coated LiCoO\textsubscript{2} between 3 and 4.8 V at the rate of 0.1 C. The coating level was estimated as \textasciitilde 1 wt %. Therefore, the capacity contribution was believed to be negligible. To understand Li conduction mechanism, Al\textsubscript{2}O\textsubscript{3}-coated LiCoO\textsubscript{2} using sputtering method was tested.\textsuperscript{20} This result showed that the independence of the Al\textsubscript{2}O\textsubscript{3} thickness on the electrochemical properties in the thin-film geometry indicated that the oxide coating layer acted as a solid electrolyte with a low electronic conductivity and a reasonably high Li-ion conductivity. In the case of the MPO\textsubscript{4}-coated cathodes, the formation of a Li-M-P-O solid-solution coating layer was expected during the cycles although the AlPO\textsubscript{4} and Sr\textsubscript{2}P\textsubscript{2}O\textsubscript{7} phases are electrochemically inactive, and CePO\textsubscript{4} is electrochemically active. As the coating thickness increases, the reaction of Li might become slower and less efficient due to the limited electronic conduction among the particles. Note that the MPO\textsubscript{4}-coated LiCoO\textsubscript{2} (M = Ce, SrH, and Fe) exhibits a large drop in the IR drop upon a 0.1 C rate discharge. This is related to the coating thickness because a similar behavior was observed in the AlPO\textsubscript{4}-coated cathodes with a coating thickness with \textasciitilde 20-50 nm.\textsuperscript{25} Hence, the FePO\textsubscript{4} with a coating thickness of \textasciitilde 20-50 nm can be influenced by the reduction in the IR drop. However, the LiCoO\textsubscript{2} that is partially covered with CePO\textsubscript{4} and SrHPO\textsubscript{4} particles was observed to have a larger IR drop than the others. This suggests that the isolated nonconducting Sr\textsubscript{2}P\textsubscript{2}O\textsubscript{7} and CeO\textsubscript{2} particles play a key role reducing the initial potential. In addition, the possibility that partially encapsulating the coating layers with SrHPO\textsubscript{4} and CePO\textsubscript{4}-coated cathodes contributes to such an IR drop cannot be ruled out.

The discharge capacities of the completely encapsulated FePO\textsubscript{4} and AlPO\textsubscript{4}-coated LiCoO\textsubscript{2} shows the highest discharge capacity, 230 mAh/g, and the LiCoO\textsubscript{2} cathodes with partially covered with SrHPO\textsubscript{4} and CePO\textsubscript{4} shows \textasciitilde 210 mAh/g. For example, the amount of Co dissolution after the first cycling increased in the order of bare (1053 ppm) > SrH - Ce (230 and 210 ppm) > Fe - Al (50 and 40 ppm, respectively). However, the bare sample showed the smallest capacity of 190 mAh/g. This clearly shows that the degree of coverage affects the discharge capacity, and a complete coverage was reported reduce the Co dissolution rate or any other side reactions between the particle surface and the electrolytes at the higher cutoff voltages.\textsuperscript{26} According to Aurbach et al., upon cycling or storage at the elevated temperatures, capacity loss of the LiCoO\textsubscript{2} electrodes cycled to 4.2 V was caused by the formation of surface films that covered the particles, which might electronically isolate them from each other and from the current collector.\textsuperscript{27} Similarly, such an electronically resistive surface film may form even faster and cause more rapid capacity loss when the electrode is cycled above 4.5 V than when it is cycled to 4.2 V.\textsuperscript{24} In addition, Co dissolution was accompanied by the loss of Li from the LiCoO\textsubscript{2} structure, resulting in a loss of Li insertion/extraction sites.\textsuperscript{26} This can eventually hinder the Li insertion/desertion sites and cause capacity fading. However, the amount of Co dissolution after 50 cycles reveals that that the AIPo\textsubscript{4}-coated cathode is similar to that of the FePO\textsubscript{4}-coated cathode, which is in contrast to the SrHPO\textsubscript{4} and CePO\textsubscript{4}-coated cathodes (Fig. 8). Despite this, it is interesting to note that the FePO\textsubscript{4}-coated cathodes continue to reduce to 0 mAh/g after 25 cycles while capacity fading of the SrHPO\textsubscript{4} and CePO\textsubscript{4}-LiCoO\textsubscript{2} was slow, showing 90 and 38 mAh/g, respectively, after 50 cycles (Fig. 7). Moreover, this suggests that such a rapid capacity fading of the FePO\textsubscript{4}-coated cathode did not originate from Co dissolution but from a decrease in Li mobility as a result of the coating layer.

The Li diffusivities of the bare and coated cathodes were estimated after 10, 20, 30, 40, and 50 cycles using GITT at 4.3 V. As shown in Fig. 8, the Li diffusivity of the FePO\textsubscript{4}-coated cathode rapidly decreases with cycling in contrast to the AlPO\textsubscript{4}-coated cathode. On the other hand, a trend of Co dissolution well agrees with that of the Li diffusivity in the bare, SrHPO\textsubscript{4} and CePO\textsubscript{4}-coated cathodes. Accordingly, the rapid capacity fading of the FePO\textsubscript{4}-coated cathode is due to the decreased Li diffusivity with cycling, but that of the SrHPO\textsubscript{4} and CePO\textsubscript{4}-coated cathodes correlated with the Co dissolution. However, it is expected that the higher capacity retention of the SrHPO\textsubscript{4} and CePO\textsubscript{4}-coated cathodes than the bare cathode is due to the fact that a partially formed coating layer suppresses Co dissolution. These results clearly show a much higher Li diffusivity of the coated cathodes along with excellent

![Figure 7](https://example.com/figure7.png)

**Figure 7.** Plots of (a) discharge profiles of MPO\textsubscript{4}-coated LiCoO\textsubscript{2} in coin-type half cell at 0.1 C between 4.8 and 3 V and (b) cycling number vs. discharge capacity.
capacity retention during cycling than the bare cathode, indicating that the formation of an electrically resistive film on the cathode was suppressed. Recently, Chen and Dahn reported that the cycle-life performance of LiCoO$_2$ was improved by a simple heat-treatment, due to the elimination of surface contamination on the cathode, for example, moisture, organic species, etc.\textsuperscript{33,34} However, our study found that the thermal history of the bare powders did not improve the electrochemical properties. The powder size used by Chen and Dahn is smaller than the conventional 10 $\mu$m sized powders.\textsuperscript{9,25,26}

In relation to Co dissolution, Fig. 9 shows the lattice constants $a$ and $c$, and the $c/a$ ratio of the coated cathodes (at the discharged state of 3 V) after cycles, which changes less than those of the bare cathode. During cycling, the surface of the bare cathode was damaged due to Co dissolution, and Li intercalation/deintercalation through this structurally damaged region was difficult. In contrast, the coating layer suppresses Co dissolution. Therefore, the surface region of the coated LiCoO$_2$ cathodes fully encapsulated with AlPO$_4$ and FePO$_4$ may be less damaged, compared with that of the cathodes that were partially encapsulated with SrHPO$_4$ and CePO$_4$. Furthermore, to investigate the structural changes after cycling, five peaks (0 0 3), (1 0 1), (1 0 4), (0 1 5), and (0 1 8) were fitted from the patterns.

Peak-broadening may be associated with either microstructural defects or a non-uniform distribution of local strain.\textsuperscript{36,37} The peak widths $\Delta k$ (full width at half maximum, fwhm) were fitted for each peak with a scattering vector $k = (4\pi/\lambda)\sin \theta$ using a double-peak Lorentzian function for $K_{01}$ and $K_{02}$. The effective grain size estimated from the intercept at $k = 0$ does not show any systematic changes due to the large error in the fitting process. Figure 10 shows the local strain in the cathodes before and after cycling with a charge cutoff voltage of 4.8 V, as a function of the coating material. The inset is a representative $\Delta k$ vs. $k$ plot in the SrHPO$_4$-coated sample measured at 3 V after 50 cycles. The local strain in the cathodes can be estimated from the slope of the $\Delta k$ vs. $k$ plot after subtracting the resolution function ($\Delta k_{\text{res}} = 0.076-0.00033(k(\text{nm}^{-1}))$). The local strain in the bare sample after 50 cycles increased approximately by a factor of four in comparison with the AlPO$_4$ and FePO$_4$-coated cathodes. Note that the change in the local strain is quite consistent with that of Co dissolution, increasing in the order of Al $< $ Fe $< $ Ce $< $ SrH. The analysis of local strain in Fig. 10 clearly demon-

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Figure 8. Plots of (a) Co dissolution of bare and MPO$_4$-coated LiCoO$_2$ and (b) lithium diffusivity of the bare and MPO$_4$-coated cathodes after 10, 20, 30, 40, and 50 cycles.

Figure 9. Plots of (a) the lattice constants $a$ and $c$, and (b) $c/a$ ratio (at the discharged state) in the bare and MPO$_4$-coated LiCoO$_2$ cathodes (M = Al, Fe, Ce, and SrH), after 50 cycles with 4.8 V.

Figure 10. The local strain in the cathodes before and after cycling with a charge cutoff voltage of 4.8 V, as a function of the coating material. The inset is a representative $\Delta k$ vs. $k$ plot in the SrHPO$_4$-coated sample measured at 3 V after 50 cycles.
strates that the MPO 4 -nanoparticle coating effectively suppresses the structural degradation caused by Co dissolution.

Figure 11 shows the discharge capacities of the bare and coated cathodes at 0.2 C at room temperature and after 90°C storage at 4 h at 4.6 and 4.8 V charge cutoffs. The trend of the discharge capacity is quite similar to the capacity retention at room temperature, and decreased in the order of Al < Ce < Sr < Fe < bare. In addition, severe reductions in capacity were observed at 90°C, compared with those at room temperature. It was observed that the Li metal was partially damaged and covered with some decomposed electrolyte products at 90°C. Hence, the decrease in capacity may be partly due to this effect. However, there is a good correlation between the 90°C storage data. The AlPO 4 -coated cathode shows no capacity decay at both 4.6 and 4.8 V, which is in contrast to the other coated cathodes. For example, the capacity of the CePO 4 , SrHPO 4 , and FePO 4 -coated cathodes decreased from 140, 130, and 123 mAh/g to 128, 110, and 98 mAh/g, respectively, when the charge cutoff voltage increased from 4.6 to 4.8 V. In particular, the largest capacity drop of the FePO 4 -coated cathodes was surprising. Even though this cathode shows comparable capacity to the AlPO 4 -coated cathode at room temperature, the capacity drop at 90°C may be related to other factors. Previous studies revealed that Co dissolution is concomitant with the dissolution of Li into the electrolyte, leading to the destruction of the Li x CoO 2 structure. 36 Once a uniform coating layer is present, Co dissolution should be minimized, and its value is expected to be similar to that of the AlPO 4 -coated LiCoO 2 . However, these results showed that the CePO 4 and SrHPO 4 -coated cathodes had better capacity retention than FePO 4.

To investigate the origin, the amounts of Co and Metal ion dissolution (Me = Al, Fe, Ce, and Sr) from the MPO 4 -coated LiCoO 2 were measured at 4.6 and 4.8 V after storage at 90°C for 1, 2, 3, and 4 h, as shown in Fig. 12. Fe dissolution showed the highest value, and M dissolution decreased in the order of Ce < Sr < Al, which is well consistent with that of capacity retention after 90°C storage. In addition, Co dissolution continues to increase with increasing storage time in all the coated cathodes, but AlPO 4 -coated cathode shows the lowest amount Co dissolution. For example, the FePO 4 -coated LiCoO 2 shows a six times larger amount of dissolution than AlPO 4 -coated cathode. This suggests that, capacity retention at 90°C is governed by M dissolution in contrast to that at room temperature. It is interesting to note that the SrHPO 4 and CePO 4 showed less Co and M dissolution than FePO 4. This is due to the lower Sr and Ce dissolution rate than Fe. This result indicates that Sr and Ce ions are relatively stable at higher temperatures than Fe ions. When the Co dissolution time was extended to 24 h, there was clearer evidence that the metal phosphate coatings minimized the Co dissolution except for the FePO 4 -coated cathode. The amounts of Co dissolution from the bare, AlPO 4 -coated, CePO 4 -coated, SrHPO 4 -coated, and FePO 4 -coated cathodes increased from 32,000, 4,400, 7,000, 7,900, and 65,000 ppm, respectively, to 98,700, 5,000, 9,500, 10,000, and 65,000 ppm, respectively.

Conclusions

The coating coverage on the LiCoO 2 cathode strongly depends on the MPO 4 nanoparticle size and morphology even though the same coating concentration was used. Hence, FePO 4 and AlPO 4 with particle sizes smaller than 20 nm exhibited complete encapsulation compared with SrHPO 4 and CePO 4, which had isolated coating layers. More surprisingly, the SrHPO 4 and CePO 4 -coated cathodes showed better capacity retention than FePO 4 at 90°C storage. This was attributed to the continuous Fe metal ion dissolution at 90°C at the highly delithiated Li x CoO 2, and a higher amount of Fe ions was dissolved into the electrolytes than the SrHPO 4 and CePO 4-coated cathodes. Therefore, the elevated temperature performance of the coated cell was influenced by the metal ion in the MPO 4 in contrast to that at room temperature. In conclusion, an AlPO 4 coating with a particle size and coating thickness <3 nm and <10-15 nm, respectively, showed the best electrochemical performance.

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